

# Weak Intermolecular Anion– $\pi$ Interactions in Pentafluorobenzyl-Substituted Ammonium Betaines

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A series of ammonium–carboxylate and ammonium–sulfonate betaines was synthesized and studied by single-crystal X-ray diffraction analysis to investigate the weak intermolecular interactions as well as the intramolecular interactions in the solid state. None of the expected intramolecular anion– $\pi$  interactions could be observed, probably because of the

steric demands and the reduced nucleophilicity of the anionic part of the betaines. Nevertheless, a weak intermolecular anion– $\pi$  interaction between the anionic part of the betaine and the pentafluorophenyl unit is present in the structure of **5a**.

## Introduction

Supramolecular chemistry is commonly defined as the chemistry of the noncovalent bond.<sup>[1]</sup> Noncovalent interactions can vary dramatically in their strength from strong electrostatic to weak dispersive attraction. They can even be repulsive. Because of their biological and chemical relevance, noncovalent interactions involving aromatic systems, such as  $\pi$ – $\pi$  stacking or cation– $\pi$  interactions, play a crucial role.<sup>[2]</sup> Recently, theoretical as well as crystallographic studies showed that the interaction between anions and electron-deficient arenes is attractive.<sup>[3]</sup> This led to intense studies in the field of anion recognition aimed at using anion– $\pi$  interactions for the development of superior anion receptors.<sup>[4]</sup> While the existence of anion– $\pi$  interactions in solid phase is broadly accepted, the relevance of anion– $\pi$  interactions in solution<sup>[4]</sup> or in the gas phase<sup>[5]</sup> remains an open question.

We started our work on anion– $\pi$  interactions in 2008.<sup>[6]</sup> First results showed that the position of an anion above the electron-deficient pentafluorophenyl unit in phosphonium and ammonium salts is flexible and can be controlled by directing substituents.<sup>[7]</sup> Moreover, we were able to prove that anion– $\pi$  interactions depend on the fluorination degree of the phenyl group. When the number of fluorine atoms at the arene is successively reduced, its electron density is enhanced. Thereby, the attractive anion– $\pi$  interaction turns

into a repulsive force.<sup>[8]</sup> Additionally, the effect of the anion geometry on the interaction of pentafluorophenyl ammonium cations with halides, nitrate, tetrafluoroborate, and hexafluorophosphate were investigated. However, no dependence of the anion– $\pi$  interaction on the geometry of the studied anions could be found in the solid state.<sup>[9]</sup> Attempts to synthesize and crystallize an ammonium hydroxide salt within this series, by substituting the *para* fluorine atom with a hydroxy group, led to the corresponding phenolate betaine **1** (Figure 1).<sup>[9]</sup>

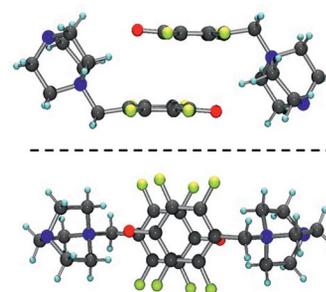


Figure 1. Crystal structure of tetrafluorophenolate betaine **1**. The cocrystallized methanol molecules were omitted for clarity. C (black), H (white), F (green), N (blue), O (red).<sup>[9]</sup>

This observation raises the following question: Could betaine structures manifest intramolecular anion– $\pi$  interactions in the solid state, or are other interactions, such as electrostatics, C–H $\cdots$ O hydrogen bonds,  $\pi$ – $\pi$  stacking, or C–H $\cdots$  $\pi$  interactions, overruling the weaker anion– $\pi$  interactions?

## Results and Discussion

To study intramolecular anion– $\pi$  interactions of pentafluorobenzyl ammonium betaines in the solid state, a series

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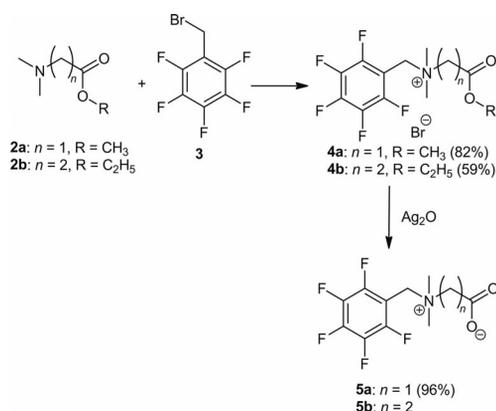
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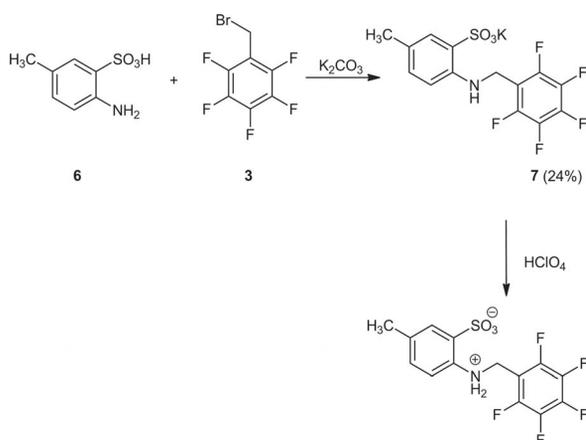
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of promising betaine structures was synthesized. Therefore, the dimethylamine carboxylesters **2a** and **2b** were treated with pentafluorobenzyl bromide (**3**) in diethyl ether to obtain the corresponding pentafluorobenzyl dimethylammonium bromides **4a** and **4b** (Scheme 1). After treatment with silver(I) oxide, the desired betaine **5a** could be isolated. Betaine **5b** could not be obtained in pure form. Attempts to purify the resulting waxy solid failed.

Scheme 1. Synthesis of the betaines **5a** and **5b**.

A more rigid betaine was synthesized by starting from 2-amino-5-methyl-phenyl sulfonic acid (**6**). After the reaction of **6** with pentafluorobenzyl bromide (**3**) and a following treatment with perchloric acid, the betaine **8** was obtained (Scheme 2).

Scheme 2. Synthesis of betaine **8**.

A series of crystals (**4a**, **4b'**, **5a**, **8**) suitable for x-ray diffraction analyses could be obtained and was analyzed with respect to anion- $\pi$  interactions in the solid state.

### Pentafluorobenzyl Dimethylammonium Carboxylesters **4a** and **4b**

Bromide salts **4a** and **4b** show structural similarities. Since compound **4b** was crystallized from wet methanol, a 1:1 mixture **4b'** of a methyl ester bromide (Figures 2c and d) and a bromide of the corresponding acid methanol solvate was obtained. However, both in **4a** and **4b'**, the bromide

anion is fixed by CH-anion interactions above the  $\pi$  system, because the carboxyl end does not seem to be involved in anion- $\pi$  contacts [**4a**:  $d(\text{CH}_2 \cdots \text{Br}) = 2.85 \text{ \AA}$  and  $d(\text{CH}_3 \cdots \text{Br}) = 2.86 \text{ \AA}$ ; **4b'**:  $d(\text{CH}_3 \cdots \text{Br}) = 2.96$  and  $3.06 \text{ \AA}$ ]. The  $\text{C}_{\text{Ar}} \cdots \text{Br}$  distances are in the range of the van der Waals (vdW) radii [**4a**:  $d(\text{C}_{\text{Ar}} \cdots \text{Br}) = 3.64\text{--}3.99 \text{ \AA}$ ; **4b'**:  $d(\text{C}_{\text{Ar}} \cdots \text{Br}) = 3.58\text{--}3.82 \text{ \AA}$ ] of the involved atoms, and because of the short distances from the anion to the centre of the aromatic moiety ( $3.57 \text{ \AA}$  for **4a** and  $3.44 \text{ \AA}$  for **4b'**) the interaction can be described as a  $\eta^6$  anion- $\pi$  interaction. In contrast to **4b'**, where all pentafluorophenyl units are parallel oriented, in **4a** the electron-deficient arenes interact with each other in a T-shape fashion. The angle between the planes of the interacting arenes is  $45.2^\circ$ , and the closest distances  $d(\text{F} \cdots \text{Centre}_{\text{Ar}})$  between the fluorine atoms F4 and F5 of one arene and the centre of another arene are  $3.28$  and  $3.71 \text{ \AA}$  (Figure 2).

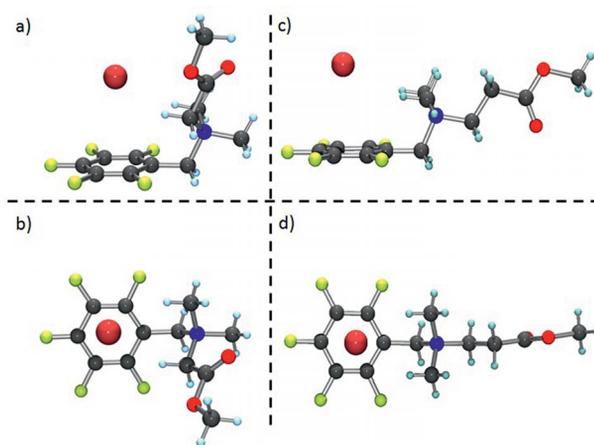
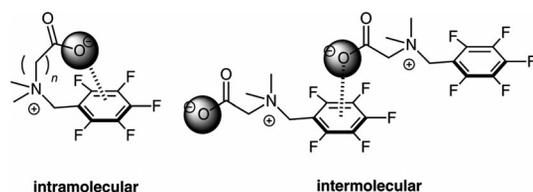


Figure 2. Two views of the ion pairs in the crystals of **4a** [side view (a) and top view (b)] and of **4b'** [(c) and (d)] showing the methyl ester bromide. The corresponding acid in the crystal structure of **4b'** is not shown. C (black), H (white), F (green), N (blue), O (red), Br (dark red).

### Pentafluorobenzyl Dimethylammonium Carboxy Betaines **5a** and **5b**

After the removal of the alkyl groups from the esters, the resulting betaines were crystallized. Betaines are able to interact both inter- and intramolecularly in the crystal structure. In which fashion they interact depends on a complex interplay of different noncovalent interactions as well as steric and electronic effects. Scheme 3 exemplifies the different orientations of the betaine units in the solid phase.

In the crystal structure of **5a** no intramolecular anion- $\pi$  interaction can be observed. One oxygen atom of the carboxyl group is fixed by CH-anion interactions [ $d(\text{CH} \cdots \text{O}) = 2.29$  and  $2.56 \text{ \AA}$ ] above the pentafluorophenyl moiety of another betaine unit (Figure 3a). The distance to the centre of the  $\text{C}_6\text{F}_5$  unit is  $3.15 \text{ \AA}$ , which is quite short. Because of the short carbon-oxygen distances of three carbon atoms [ $\text{C4-C6}$ ,  $d(\text{C} \cdots \text{O-R}) = 3.06$ ,  $3.25$ , and  $3.27 \text{ \AA}$ ], the interaction can be described as a  $\eta^3$  anion- $\pi$  contact.



Scheme 3. Possible anion- $\pi$  interactions in the solid state: intra- vs. intermolecular interactions.

An examination of the molecular packing of the betaine units reveals a  $\pi$ - $\pi$  stacking of the fluorinated arenes with a plane-to-plane distance of 3.24 Å (Figure 3b).

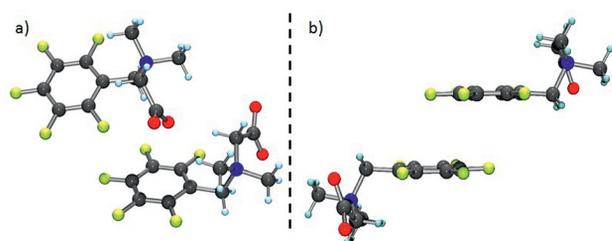


Figure 3. A top and a side view of neighbouring betaine molecules in the crystal structure of **5a**, showing (a) the anion- $\pi$  as well as (b) the  $\pi$ - $\pi$  stacking interactions. C (black), H (white), F (green), N (blue), O (red).

In contrast to our expectation, an intramolecular anion- $\pi$  interaction was not observed in the crystal structure of **5a**. This might be due to the insufficient length of the alkyl chain between the pentafluorophenyl and the carboxyl group. Therefore, the derivative **5b** was synthesized with a longer alkyl spacer. The resulting product could not be purified, and because of its highly hygroscopic nature, no crystals could be obtained for **5b**.

## 2-(Pentafluorobenzyl)ammonium-5-methylphenyl Sulfonate Betaine **8**

A more rigid and better preorganized betaine for an intramolecular anion- $\pi$  interaction is **8**. First attempts to isolate the betaine by the treatment of the potassium salt **7** with perchloric acid and the subsequent crystallization from a mixture of DMF and ethyl ether led to crystals of the potassium salt **7**. The crystal structure of **7**, containing three organic anions, three potassium cations, and three DMF molecules in an asymmetric unit, did not reveal an anion- $\pi$  interaction between the sulfonate group and the pentafluorophenyl unit (Figure 4). Because of the interactions between the sulfonate groups and the potassium cations [ $d(\text{K}\cdots\text{OSO}_2\text{-R}) = 2.69\text{--}2.86$  Å], they are turned away from the electron-deficient moiety. Two molecules of DMF were found in the coordination sphere of each potassium ion [ $d(\text{K}\cdots\text{O}_{\text{DMF}}) = 2.56\text{--}2.76$  Å]. Between the fluorinated arenes, a shifted face-to-face contact with a closest  $\text{C}_{\text{Ar}}\cdots\text{C}_{\text{Ar}}$  distance of 3.42 Å was observed. Intramolecular N-H $\cdots$ O interactions were also found (see Table 1).

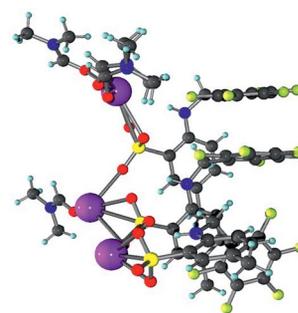


Figure 4. Part of the crystal structure of the potassium salt **7**. C (black), H (white), F (green), N (blue), O (red), S (yellow), K (violet).

Table 1. Hydrogen bonds in **7** and **8**.

Structure	D-H $\cdots$ A	$d(\text{D}\cdots\text{A})$ [Å]	$\angle(\text{D-H}\cdots\text{A})$ [°]
<b>7</b>	N1-H1 $\cdots$ O1	2.984(4)	123(3)
<b>7</b>	N1A-H1A $\cdots$ O1A	2.820(4)	137(3)
<b>7</b>	N1B-H1B $\cdots$ O1B	2.985(4)	125(3)
<b>8</b>	N1-H1A $\cdots$ O2	2.718(3)	172(2) <sup>[a]</sup>
<b>8</b>	N1-H1B $\cdots$ O1	2.747(3)	139(2)
<b>8</b>	N1-H1B $\cdots$ O1	2.874(3)	131(2) <sup>[b]</sup>
<b>8</b>	C7-H7A $\cdots$ O2	3.369(3)	141.7

[a] Symmetry operations  $x, y + 1, z$ . [b] Symmetry operations  $x + 1, y + 1, z + 1$ .

Further attempts to crystallize compound **8** finally resulted in the solid-state structure of the desired betaine (Figure 5). Unfortunately, the structure shows no intramolecular anion- $\pi$  interactions. The crystal packing reveals that two adjacent molecules are oriented parallel to each other, whereby the sulfonate group of one molecule interacts with the  $\text{C}_6\text{F}_5$  unit of the other [ $d(\text{C}\cdots\text{OSO}_2) = 2.98\text{--}4.29$  Å]. Thereby, two oxygen atoms of each sulfonate unit are within the range of the vdW radii of the involved atoms. However, these anion- $\pi$  contacts are induced by much stronger NH $\cdots$ O hydrogen-bonding interactions between ammonium and sulfonate groups (see Table 1 and Figure 5b). Anion- $\pi$  interactions are not required to stabilize this structure, but they cannot be ruled out. There is also a weak intramolecular CH $\cdots$ O contact.

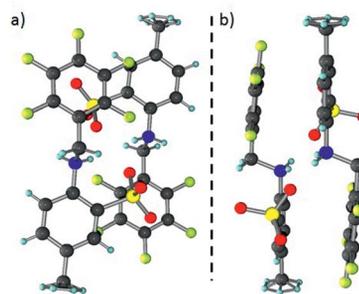


Figure 5. Top and side view of two adjacent betaine molecules in the solid-state structure of **8**. C (black), H (white), F (green), N (blue), O (red).

The absence of intramolecular interactions of the anionic part of the betaine with the electron-deficient arene can be

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explained by the influence of the crystal packing. For an intramolecular interaction, the betaine molecule has to bend into a spherical shape. However, to achieve a closest packing of the molecules, the linear shape with its intermolecular anion- $\pi$  interaction seems to be favoured. Moreover, because of the close packing of the betaine units in the solid state, the difference between an intra- and an intermolecular anion- $\pi$  interaction is small. In solution, the intramolecular interaction should be entropically favoured over the intermolecular one. Attempts to investigate the interplay of inter- and intramolecular anion- $\pi$  interactions in solution failed.

## Conclusions

In conclusion, the present study shows that betaines exhibit anion- $\pi$  interactions in the solid state. The expected intramolecular interaction could not be observed. The intramolecular interaction prevents an efficient close packing, and therefore the intermolecular anion- $\pi$  interaction might be favoured. Further investigations with structurally optimized betaines will have to be performed to determine whether an internal anion- $\pi$  interaction is possible and will elucidate the interplay of intra- and intermolecular anion- $\pi$  interactions in solution.

## Experimental Section

All commercially available reagents were used as received. Solvents were distilled and used without further purification.  $^1\text{H}$  (300 MHz) and  $^{19}\text{F}$  (300 and 400 MHz) NMR spectra were obtained with a Varian Mercury 300 or Inova 400 spectrometer in deuterated solvents. The mass spectrometric data were recorded with a Finnigan SSQ 7000 and a Thermo Deca XP system by using EI (70 eV) or ESI, and the infrared spectra were measured with a PerkinElmer FTIR spectrometer (Spectrum 100). The samples were measured in KBr (4000–650  $\text{cm}^{-1}$ ). Elemental analyses were performed with a CHN-O-Rapid Vario EL system from Heraeus. The melting points were measured with a Büchi B-540 system and were not corrected. X-ray diffraction analyses are described at the end of the Experimental Section.

**Synthesis of Pentafluorobenzyl Ammonium Bromides 4a and 4b:** Equimolar amounts of pentafluorobenzyl bromide and the corresponding dimethyl carboxyl esters (*N,N*-dimethylglycine methyl ester or *N,N*-dimethyl- $\beta$ -alanine ethyl ester) were dissolved in hexane (10 mL). After the evaporation of the solvent, the obtained solid was dried under vacuum.

**4a:** Colourless solid (2.41 g, 6.3 mmol, 82% yield). M.p. 197 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 300 MHz):  $\delta$  = 5.02 (s, 2 H,  $\text{CH}_2$ ), 4.60 (s, 2 H,  $\text{CH}_2$ ), 3.89 (s, 3 H,  $\text{CH}_3$ ), 3.32 (s, 6 H,  $\text{CH}_3$ ) ppm.  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{OD}$ , 300 MHz):  $\delta$  = -137.95 (m, 2 F,  $F_{ortho}$ ), -150.77 (m, 1 F,  $F_{para}$ ), -162.63 (m, 2 F,  $F_{meta}$ ) ppm. MS (ESI):  $m/z$  (%) = 298.5 (100)  $[\text{M}]^+$ ,  $\text{C}_{12}\text{H}_{13}\text{F}_5\text{NO}_2^+$ . IR (KBr):  $\tilde{\nu}$  = 3056 (w), 3012 (m), 2949 (m), 2444 (w), 2043 (w), 2000 (w), 1750 (vs), 1659 (m), 1588 (w), 1556 (w), 1508 (vs), 1431 (m), 1397 (m), 1347 (w), 1312 (m), 1254 (m), 1231 (m), 1203 (vs), 1133 (vs), 1061 (m), 1013 (s), 983 (m), 960 (vs), 944 (s), 914 (m), 872 (s), 778 (w), 745 (m), 718 (w), 678 (m)  $\text{cm}^{-1}$ .  $\text{C}_{12}\text{H}_{13}\text{BrF}_5\text{NO}_2$  (377.00): calcd. C 38.12, H 3.47, N 3.70; found C 38.08, H 3.45, N 3.72.

**4b:** Colourless solid (182 mg, 0.5 mmol, 59% yield). M.p. 52 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 5.13 (s, 2 H,  $\text{H}_{benzyl}$ ), 4.16 (q,  $J$  = 7.1 Hz, 2 H,  $\text{CH}_2$ ), 4.10 (t,  $J$  = 7.1 Hz, 2 H,  $\text{CH}_2$ ), 3.50 (s, 6 H,  $\text{CH}_3$ ), 3.10 (t,  $J$  = 7.1 Hz, 2 H,  $\text{CH}_2$ ), 1.26 (t,  $J$  = 7.1 Hz, 3 H,  $\text{CH}_3$ ) ppm.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = -134.13 (m, 2 F,  $F_{ortho}$ ), -145.33 (m, 1 F,  $F_{para}$ ), -157.83 (m, 2 F,  $F_{meta}$ ) ppm. MS (ESI):  $m/z$  (%) = 326.0 (100)  $[\text{M}]^+$ ,  $\text{C}_{14}\text{H}_{17}\text{F}_5\text{NO}_2^+$ . IR (KBr):  $\tilde{\nu}$  = 3425 (w), 2965 (m), 2660 (w), 2462 (w), 2083 (w), 1945 (w), 1728 (vs), 1659 (m), 1507 (vs), 1427 (w), 1376 (m), 1334 (m), 1309 (m), 1200 (s), 1133 (s), 1093 (w), 1028 (s), 973 (s), 891 (m), 854 (w), 804 (m), 737 (w), 681 (m)  $\text{cm}^{-1}$ .  $\text{C}_{14}\text{H}_{17}\text{BrF}_5\text{NO}_2 \cdot 1/3\text{H}_2\text{O}$  (406.19): calcd. C 40.79, H 4.32, N 3.40; found C 40.71, H 4.00, N 3.48.

**Synthesis of Pentafluorobenzyl Ammonium Betaines 5a:** The pentafluorobenzyl ammonium bromide **4a** (1.00 g, 2.65 mmol) was dissolved in water (10 mL), and 1.0 equiv. of silver(I) oxide (373 mg, 2.65 mmol) was added. The suspension was stirred for 12 h in the dark. The precipitate was filtered off. The solvent was removed, and the remaining white solid was dried under vacuum.

**5a:** Colourless solid (720 mg, 2.5 mmol, 96% yield). M.p. 225 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 300 MHz):  $\delta$  = 5.07 (s, 2 H,  $\text{CH}_2$ ), 3.96 (s, 2 H,  $\text{CH}_2$ ), 3.32 (s, 6 H,  $\text{CH}_3$ ) ppm.  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{OD}$ , 300 MHz):  $\delta$  = -137.84 (m, 2 F,  $F_{ortho}$ ), -151.85 (m, 2 F,  $F_{para}$ ), -163.12 (m, 2 F,  $F_{meta}$ ) ppm. MS (ESI):  $m/z$  (%) = 283.9 (100)  $[\text{MH}]^+$ ,  $\text{C}_{11}\text{H}_{10}\text{F}_5\text{NO}_2^+$ . IR (KBr):  $\tilde{\nu}$  = 3355 (w), 3024 (w), 2996 (w), 2963 (w), 2198 (w), 2066 (w), 1993 (w), 1626 (vs), 1523 (s), 1503 (vs), 1428 (m), 1387 (s), 1370 (m), 1326 (s), 1213 (w), 1156 (w), 1133 (s), 1058 (m), 1014 (m), 961 (s), 919 (m), 896 (s), 883 (s), 774 (w), 708 (m), 682 (m)  $\text{cm}^{-1}$ .  $\text{C}_{11}\text{H}_{10}\text{F}_5\text{NO}_2$  (283.19): calcd. C 45.21, H 3.79, N 4.79; found C 45.42, H 3.56, N 4.92.

**Synthesis of Potassium Pentafluorobenzyl-2-amino-5-methylphenyl Sulfonate (7):** To a solution of 2-amino-5-methylphenyl sulfonic acid (144 mg, 0.82 mmol) in DMF (10 mL) were added pentafluorobenzyl bromide (200 mg, 0.82 mmol) and potassium carbonate (424 mg, 3.11 mmol). The mixture was stirred for 12 h at room temperature. After evaporation of the solvent, the remaining white solid was redissolved in chloroform. The insoluble salts were filtered off, and the solvent was removed. The obtained solid was dried under vacuum. Colourless solid (78 mg, 0.2 mmol, 24% yield). M.p. 138 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz):  $\delta$  = 7.96 (s, 2 H,  $\text{H}_{benzyl}$ ), 7.51 (s, 1 H,  $\text{H}_{aryl}$ ), 7.07 (d,  $J$  = 8.6 Hz, 1 H,  $\text{H}_{aryl}$ ), 6.79 (d,  $J$  = 8.6 Hz, 1 H,  $\text{H}_{aryl}$ ), 4.51 (s, 3 H,  $\text{CH}_3$ ) ppm.  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz):  $\delta$  = -145.18 (m, 2 F,  $F_{ortho}$ ), -159.20 (m, 1 F,  $F_{para}$ ), -165.54 (m, 2 F,  $F_{meta}$ ) ppm. MS (ESI):  $m/z$  (%) = 365.9 (100)  $[\text{M}]^+$ ,  $\text{C}_{14}\text{H}_9\text{F}_5\text{NO}_3\text{S}^-$ . IR (KBr):  $\tilde{\nu}$  = 3368 (w), 3033 (w), 2929 (w), 2736 (w), 2443 (w), 2215 (w), 2164 (w), 2118 (w), 2076 (w), 2044 (w), 2011 (w), 1983 (w), 1931 (w), 1844 (w), 1659 (s), 1617 (m), 1501 (vs), 1407 (m), 1366 (m), 1321 (m), 1261 (m), 1184 (vs), 1102 (s), 1073 (m), 1027 (vs), 938 (s), 887 (w), 810 (s), 701 (s), 663 (m)  $\text{cm}^{-1}$ .  $\text{C}_{14}\text{H}_9\text{F}_5\text{KNO}_3\text{S} \cdot 1/2\text{DMF} \cdot 3/2\text{H}_2\text{O}$  (405.38): calcd. C 39.70, H 3.33, N 4.48; found C 39.80, H 3.24, N 4.40.

**Synthesis of Potassium Pentafluorobenzyl-2-ammonium-5-methylphenyl Sulfonate (8):** Potassium pentafluorobenzyl-2-amino-5-methylphenyl sulfonate (200 mg, 0.5 mmol) was dissolved in methanol (6 mL), and perchloric acid (70%, 70 mg, 0.49 mmol, 1.0 equiv.) was added. The precipitating white solid was filtered off, and crystals were directly grown by slow evaporation of the solvent.

## Single-Crystal X-ray Analyses

Single-crystal X-ray diffraction data were collected at 123(2)°K using a Bruker-Nonius KappaCCD diffractometer with an APEX-II detector and graphite monochromated  $\text{Mo-K}\alpha$  ( $\lambda$  = 0.71073 Å) radiation. COLLECT<sup>[10a]</sup> software was used for the data collection

( $\theta$  and  $\omega$  scans) and DENZO-SMN software<sup>[10b]</sup> for the processing. The structures were solved by direct methods with SIR2004 software<sup>[10c]</sup> and refined by full-matrix least-squares methods with WinGX software,<sup>[10d]</sup> which utilizes the SHELXL-97 module.<sup>[10e]</sup> A Lorentzian polarization correction was applied to all data, and absorption effects were corrected with a multi-scan method (SADABS software<sup>[10f]</sup>), except for **5a**. All C-H hydrogen positions were calculated and refined by using a riding-atom model, except for disordered formyl H atoms in DMF molecules in **7**. Hydrogen atoms bonded to N, O, or C atoms (including the mentioned formyl H atoms) were found by using Fourier maps and fixed (by using the command DFIX,  $s = 0.02$ ) to a distance of 0.91 Å from the N atoms, 0.84 Å from the O atoms, and 0.95 Å from the C atoms. The thermal parameters of noncalculated H atoms were set to values 1.2 times those of the C or N atoms they are bound to, and they were set to values 1.5 times those of the O atoms they were bound to. Disorder in geometry was restrained by using the commands SADI (for **4b**,  $s = 0.02$ ) or SAME (for **7**,  $s1 = 0.02$ ), and disorder in anisotropic parameters was restrained by using the commands EADP (for the N atom of disordered DMF in **7**), SIMU (for **4a** and **7**,  $s = 0.01$ ), DELU (for **7**,  $s1 = 0.01$ ), and ISOR (for **4b** and **7**,  $s = 0.01$ ) in final refinement cycles.

CCDC-868496 (for **4a**), -868497 (for **4b'**), -868498 (for **5a**), -868499 (for **7**), and -868500 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see footnote on the first page of this article): Summary of crystallographic data and parameters.

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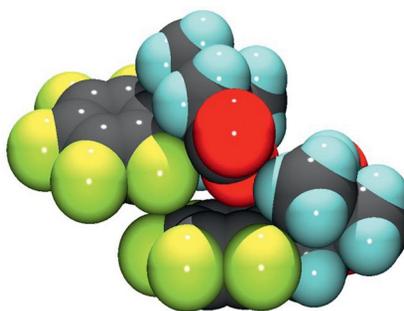
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A series of betaines bearing pentafluorobenzyl groups was synthesized and investigated with respect to intra- and intermolecular interactions in the solid state. The carboxylic end of betaine **5a** interacts with the electron-deficient arene of a neighbouring molecule in the solid phase.



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K. Rissanen ..... 1–6

Weak Intermolecular Anion- $\pi$  Interactions  
in Pentafluorobenzyl-Substituted Ammonium  
Betaines 

**Keywords:** Anion- $\pi$  interactions / Betaines /  
X-ray structures / Supramolecular chemistry /  
Noncovalent interactions